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APR 82 F R MAYO, S E BUTTRILL, R LAN

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20. ABSTRACT CONTINUED

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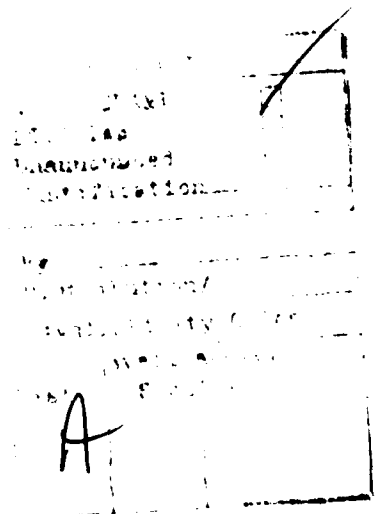
BASIC STUDY OF FUEL STORAGE STABILITY

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I INTRODUCTION

The object of this work is to determine the mechanism by which gum and deposits are formed in diesel fuels, and thus how to predict and prevent their formation. We have been following the development of deposit precursors during oxidations of pure hydrocarbons at 130°C by field ionization mass spectrometry (FIMS), and also testing high performance liquid chromatography (HPLC) for the same purposes. HPLC might be a convenient and economical substitute for FIMS.

The previous report, Interim Report No. 1 (March 22, 1982), included all useful data on this project since the joint Final Report of October 1, 1981 to NASA-Lewis and ARO. The present report includes data on deposit formation and rates of oxidation of several diesel fuels supplied by the U.S. Army Fuels and Lubricants Research Laboratory at San Antonio, done during the previous year, which have not yet appeared in any written report.

II TECHNICAL PROGRESS SUMMARY

The oxidation of 1-phenylhexane was initially faster than that of n-dodecane but does not appear to be autocatalytic, as shown in the last report. We have since found that there are 26.1 milliequivalents of hydroperoxide formed per initial mole 1-phenylhexane (or 0.1611 meq. of peroxide/g) at the end of the reaction, 10 hrs. For the 19.6 mmole of O₂/gm taken up, only 0.82% of the oxygen absorbed is found as peroxide. Residual gum was 1.5761 mg, 18.54 mg/100 gm fuel, representing 0.0185% of the initial 1-phenylhexane.

In the search for pure aliphatic hydrocarbons that might give deposits, bicyclohexyl was oxidized in air at 130°C. The oxidation rate was unexpectedly slow up to 400 hours, when 29 μ moles of O₂ was absorbed per gram bicyclohexyl, but then increased substantially so that 25 μ moles was absorbed in the next 75 hours. The sample becomes glassy on storage in a freezer. Tests are in progress to determine the products of the oxidation.

Gum determinations were carried out for both freshly distilled and

undistilled Fuel 10. Multiple determinations were performed for each fuel sample. The mean and standard deviations were calculated as shown in Table 1.

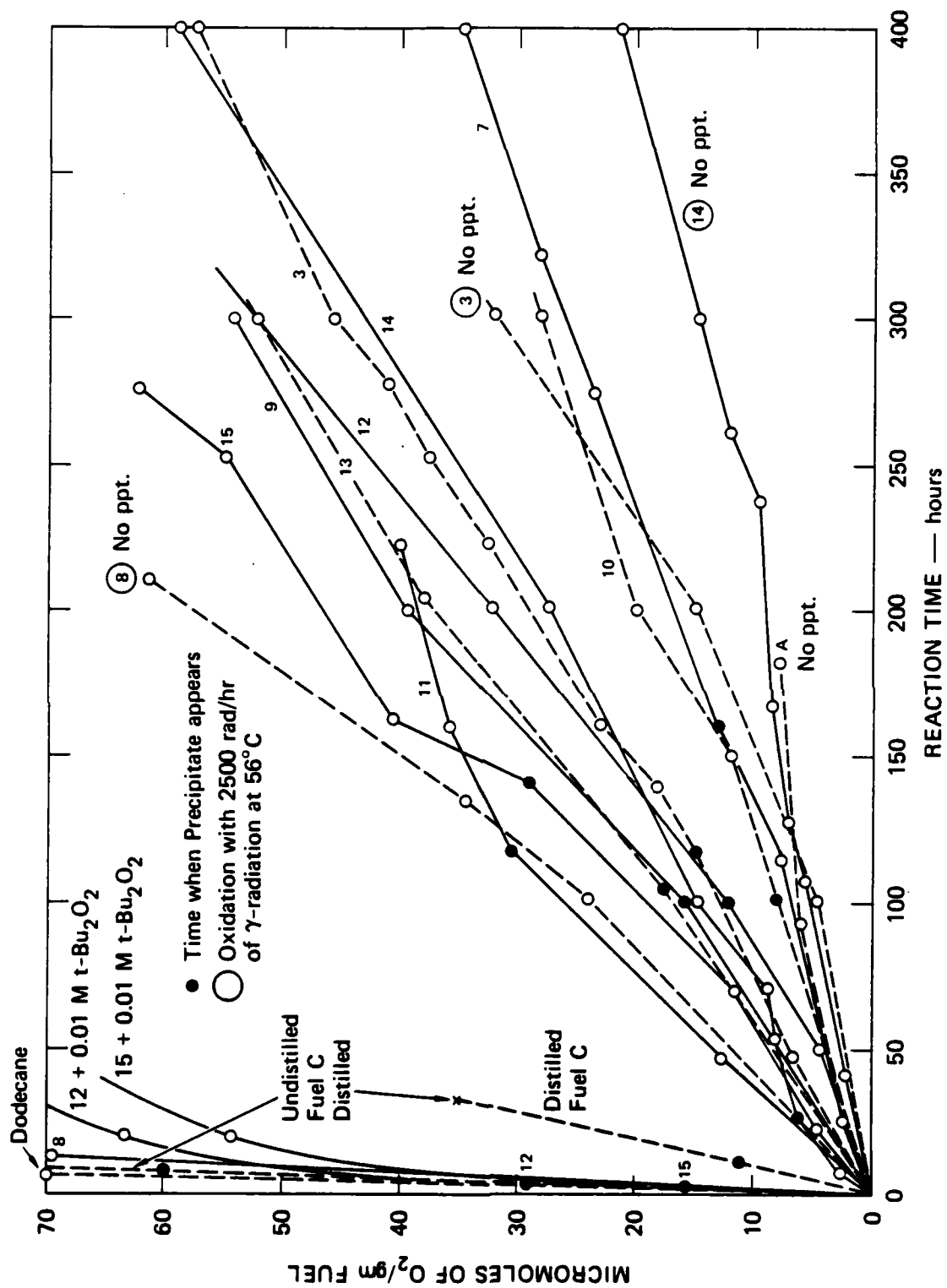
Table 1
GUM DETERMINATION ON DIESEL FUEL 10

	<u>Mg/100 gm fuel</u>	<u>Mean</u>	<u>Standard Deviation</u> <u>mg/100 gm</u>
Freshly distilled	.484		
	.409		
	.539	0.573	0.139
	.709		
	.726		
Undistilled	11.756		
	13.087	12.765	0.854
	13.7578		
	12.4499		

The relative errors are smaller with higher gum contents. We are in the process of improving our technique. One problem was the use of home-made aluminum boats that contain creases. Losses occur due to capillary action with acetone creeping over the edge of the boat. We have recently located a source of factory-made aluminum boats for microbalances that have a smooth surface and meet our weight requirements.

Figure 1 summarizes data on rates of oxidation of ten diesel fuels obtained from the U.S. Army Fuels and Lubricants Laboratory at San Antonio. So that the properties of the fresh rather than aged (with unknown histories) fuels could be determined, all were distilled in vacuum, with the results shown in Table 2, and stored under nitrogen and refrigeration.

In general, Figure 1 shows oxygen absorption, measured by gas chromatography, as a function of oxidation time under air at 130°C for the numbered diesel fuels. The solid points indicate where precipitation of sediment was first observed. Data are also included for jet turbine fuels A (stable) and C (unstable) in the NASA-Lewis Program, and for



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FIGURE 1 OXYGEN CONSUMPTION BY FUELS AT $130^\circ C$

Table 2

VACUUM DISTILLATIONS OF DIESEL FUELS

Fuel# ^a	Pressure torr	Boiling Range, °C			Notes
		Initial	~65%	Final	
A	5	48	72	90	Clear, colorless
C	5	35	95	110	First distillation, yellow Pale yellow after redistillation
3	16	65	168	227	
4	16	54-66	182	225	
7	17	50	120	140	
8	18	80	113	142	
9	17	50	140	150	
10	15	50	100	105	Reddish, Redistilled
10	22	60	161	215	
11	17	45	140	227	
12	11.5	55	100	150	Slightly yellow, redistilled
13	3	36	92	120	Slightly yellow
13	7.5	55	110	120	Redistilled, clear
14	16	48-58	187	222	
14	5	50	90	100	
15	12	55	130	145	

^aBrown bottle stored in freezer

n-dodecane (of interest in both programs).

Figure 1 shows a wide range of rates of oxidation. Deposits appeared in most fuels at about 100 to 150 hours, but over a considerable range of oxygen absorption. Fuel 8 and dodecane, which oxidized the fastest, gave no deposits. The stable jet turbine Fuel A also gave no deposits. Addition of 0.01 M t-Bu₂O₂ to fuels 12 and 15 greatly accelerated rates of oxygen absorption but had no large effect on the amount of oxygen consumed at the point where deposits appeared. Fuel C, the dirtiest fuel, oxidized fairly rapidly and had absorbed the least oxygen when deposits appeared. Thus, there is no obvious correlation between rate of oxygen absorption and sediment formation.

Curves with fuel numbers in circles were oxidized at 56°C with 2500 rad/hr of γ -radiation. The radiation made the oxygen absorption at 56° about half as fast as at 130°, but no deposits appeared in any of the radiated runs. We conclude that the oxidation process, but not the condensation process, in gum formation is accelerated by radiation, and that radiation experiments alone are no guide to gum or deposit formation.

III WORK PLANNED

1. Efforts will be directed to the refinement of our gum determination method. New aluminum boats without creases will be used and adjustments made on the evaporating procedures. A report on the method will be written for evaluation as soon as possible.
2. We will investigate the bicyclohexyl oxidation further to determine the significance of the low rate, to check for dimer and trimer formation, to extend the oxidation time.
3. The effect of stainless steel wool, SS 316, on deposit formation from Diesel Fuel 10 will be investigated.
4. We intend to carry out one oxidation of phenylcyclohexane with 0.1 M t-BuNH₂.